

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Preparation of Organic Isocyanates.

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, located at Wilmington 98, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved chemical process, and more particularly to a process for the manufacture of organic isocyanates by the reaction of phosgene on amines.

In the formation of organic isocyanate an amine is reacted with phosgene, giving the organic isocyanate together with hydrogen chloride as a by-product. Usually an excess of the phosgene is employed so that the by-product gas is a mixture of hydrogen chloride and phosgene. The prior art discloses various methods for carrying out this process. Usually this process is carried out as a batch process and it was early disclosed that the reaction be carried out in an autoclave under autogenous pressure with subsequent venting of the gases at the end of the reaction and distillation of the organic solvent solution of the isocyanate. In a more recent process it is disclosed that the gases can be vented as the reaction proceeds, although still maintaining relatively high pressures in the autoclave. This latter process allegedly reduced the time of reaction, although in the illustrations disclosed the reaction was carried out for a period of from 45 minutes to two hours.

It is an object of the present invention to provide a continuous process for the manufacture of organic isocyanates in which the reaction is carried out and completed in a very short interval of time but which gives high yields of a product of relatively

high purity.

According to the present invention, the process of manufacturing organic isocyanates from organic amines and phosgene, includes the step of passing an inert solvent solution of an amine into an organic solvent solution of phosgene, at least 1.25 mols of phosgene being present per equivalent $-NH_2$ group, the reaction being conducted under super atmospheric pressure and under conditions of turbulent flow while maintaining the temperature above that at which the carbamyl chloride of the particular amine employed is decomposed.

In the accompanying drawing which forms a part of the specification, a diagrammatic representation of equipment in which this process may be carried out is illustrated. The reservoir may be a jacketed reservoir in which the solvent is maintained at the desired reaction temperature, or when desired the reservoir may be merely an exhaust vessel into which the reaction solution is expelled and any additional heat necessary to cause the reaction may be applied through a heater after the introduction of the amine solution into the solvent solution of the phosgene. Any solvent carried over with the hydrogen chloride and excess phosgene gases may be returned to the reservoir, or, alternatively, may be introduced with fresh solvent on the low pressure side of the pump. Where the process is carried out with no recycling of the isocyanate solvent solution, the isocyanate and solvent may be removed directly from the reservoir to a suitable still, and in this alternative fresh solvent is introduced into the low pressure side of the pump.

In the apparatus as illustrated, the solvent employed is put under pressure by the pump in the pipe line into which the phosgene is introduced either through a nozzle to break up the gas into small bubbles or by mere introduction of the gas into the

line which is flowing at a rate to assure turbulent flow in the tube. The amine solution is then introduced under necessary pressure directly into the solvent solution

5 of the phosgene and, again, at a point where the solution is in turbulent flow as it passes through the space enclosed with the heater. In the system the relationship of the rate of flow and the diameter of the pipe must
10 be such that the solvent is in turbulent flow.

This causes substantially complete solution of the phosgene in the solvent, so that the amine when introduced as a solution in the solvent, is in complete and thorough contact
15 with the phosgene in the solution.

The reaction is substantially instantaneous, for it is found, as illustrated in the following examples, that the reaction takes place in the fraction of a
20 second. The solution is then vented through a valve into the reservoir which is maintained at pressure much lower than that in the line and usually at substantially atmospheric pressure so the hydrogen chloride and
25 excess phosgene is flashed from the solution and carried off through a condenser. Any entrained solvent is thus recovered and can be returned to the system as desired.

The pressure in the reaction zone in the
30 pipe line is maintained by a valve or, as hereinafter illustrated, where the pressure used is not high it is merely maintained by the pressure the pump exerts on the solution in the line. The solvent solution of the
35 isocyanate can be recirculated through the pump to produce a higher concentration of isocyanate in the solution. After the desired concentration of isocyanate in the solution is obtained, some of the isocyanate
40 solution is continually removed to a still or storage to maintain a constant level in the reservoir and fresh solvent is added at the low pressure side of the pump. Alternatively, the isocyanate solution may be re-
45 moved directly to a still or storage and not recirculated, in which case fresh solvent, which may include that which is recovered from the condenser, is introduced into the line.

50 It has been found that by carrying out the reaction as herein disclosed there is substantially no reaction of the amine with the isocyanate even when the recycling process is employed. The amine appears to react
55 preferentially with the phosgene to form the isocyanate. If the isocyanate content of the recycle stream rises materially above 15%, some reaction of the isocyanate with the amine may take place to cause some
60 decrease in the yield of the desired isocyanate. In such case the recycle stream may be diluted by the addition of fresh solvent. The solvent flashed from the product stream along with the dissolved phosgene and
65 hydrogen chloride may be returned directly

to the system without purification.

One of the advantages of the present process is that, due to the increased solubility of phosgene in the solvent under pressure, less solvent needs to be circulated through
70 the pipe line reactor for any given quantity of amine and phosgene fed. Under the conditions of this invention the hydrogen chloride is stripped off from the solvent solution of the isocyanate at a pressure sub-
75 stantially lower than that in which the reaction takes place. This facilitates the removal of the hydrogen chloride. By adding phosgene under pressure the higher ratio of phosgene to hydrogen chloride can be main-
80 tained, which materially favors the formation of the isocyanate directly without going through the amine hydrochloride formation. It is believed that this favors the improved yields which are obtained.

85 The isocyanate is recovered by distilling off the solvent, which solvent can again be recirculated in the system. The isocyanate can then be redistilled, if desired. Both distillations are preferably carried out under
90 reduced pressure.

Pressures of from 5 to 20 pounds per square inch gauge have been found to be satisfactory for carrying out the process of this invention, although higher pressures
95 even up to 200 pounds may be employed if desired. A centrifugal pump or positive displacement pump may be used.

It is essential that the phosgene be introduced into the solvent stream so that it is
100 completely dissolved therein before the introduction of the amine solution. The molar ratio of the phosgene to amine should be such that there is at least 25% stoichiometrical excess of the phosgene, that is, one
105 should employ at least 1.25 mols of phosgene per equivalent of $-NH_2$ group of the amine. Usually a much greater excess of phosgene is employed and the preferred range would be between 70% and 110%
110 excess of phosgene. In general it is unnecessary to use an excess above 110%.

The temperature at which the reaction is carried out should be above the decomposition temperature of the intermediate car-
115 bamyl chloride formed by the reaction of phosgene with the amine. This temperature will range from 90° to 180°C., depending upon the particular amine employed. While higher temperatures may be employed, they
120 are not required. The flashing off of the hydrogen chloride as the reaction stream passes into the reservoir maintained at lower pressure permits its ready removal from the solution at these temperatures.

125 The concentration of the organic amine in the solvent should preferably be between about 5% and 30%. Below this range the amount of solvent required is unnecessarily large, and when operating materially above
130

this range of concentration the yields may be decreased by the formation of tarry by-products.

The solvents employed in this process are preferably the chlorinated aromatic hydrocarbon solvents in which the phosgene is relatively soluble under the pressures employed. It is preferred that the solvent have a lower boiling point than the particular isocyanate which is being prepared in order that the isocyanate will remain dissolved in the solution but can be readily removed therefrom by distillation of the solvent. The mono chlorobenzene, o-dichlorobenzene, p-dichlorobenzene the trichlorobenzenes, the corresponding toluenes and xylenes, chloroethylbenzene, monochlorodiphenyl and the alpha- and beta-naphthyl chloride are illustrative of the types which may be used. Because of its particular boiling point, the o-dichlorobenzene is a preferred solvent. Any other inert organic solvent, in which the phosgene and the amine are relatively soluble under the pressures used, may be employed.

The process of this invention is applicable to the manufacture of isocyanates in general which can normally be prepared by the reaction of amines with phosgene, either mono-, di- or polyisocyanates from the corresponding mono- di- and polyamines. The process is particularly applicable to the reaction of aromatic amines with phosgene, such as aniline, toluidine, benzidine, naphthyl amines, 2,4-tolylene diamine, 2,6-tolylene diamine, the phenylene diamines, 4,4'-diamino diphenyl methane, 1,5-naphthalene diamine, 1-amino-3-(4-aminophenyl) pro-

pane, anisidine or chloroanilines.

The following examples are given to more fully illustrate the invention, in which the yields given are based on the weight of the amine employed.

EXAMPLE 1.

The equipment used is arranged as in the accompanying drawing. Ortho-dichlorobenzene is used as the solvent and m-tolylene diamine is used for the preparation of 2,4-tolylene diisocyanate. The process is started with 55 parts of o-dichlorobenzene in the reservoir vessel. This is pumped through the pipe line reactor where phosgene is first introduced and then an 8% (by weight) solution of m-tolylene diamine in o-dichlorobenzene is introduced. The solution is then returned to the reservoir vessel through a valve which is adjusted to give the pressure desired.

In this equipment the reservoir is a 10 gallon jacketed enamel kettle. Heat is supplied to the jacket by a hot oil system. The pump used is a stainless steel centrifugal pump. The phosgene inlet consists of a 1/2 inch pipe brought into the recycle reaction line at a tee. The recycle reaction line is 1 inch diameter schedule 40 stainless steel pipe. The linear distance from the phosgene inlet to the diamine solution inlet is approximately 4 feet. The diamine solution inlet is at a 1 inch tee at a right angle bend in the line. The pressure relieving device is a 1 inch valve placed 8 inches downstream from the amine solution inlet. The flow and conditions of the process are as given below.

	Quantity	
Initial charge in reservoir, o-dichlorobenzene	55 lbs.	
m-Tolylene diamine in feed	8%	
Temperature of m-tolylene diamine feed soln.	110°C.	
Rate of addition of m-tolylene diamine	3.15 lbs./hr.	
Rate of addition of phosgene	10.0 lbs./hr.	
Rate of recycle feed through pump	8 gals./min.	
Velocity in reaction zone, linear	3 ft./sec.	
Temperature in reaction zone	165°C.	
Temperature in reservoir kettle	165°C.	
Pressure in reservoir kettle	Atmospheric	
Pressure in reaction line	8 p.s.i. gauge	
Excess phosgene employed (above theory)	96%	
Time of run	3 hours	
Yield of 2,4-tolylene diisocyanate	90.5%	

When methylene bis(4-phenylamine) is substituted for m-tolylene diamine in molar equivalent amount, methylene bis(4-phenyl isocyanate) is obtained in similar yield.

Benzidine similarly gives 4,4'-diphenyl

diisocyanate in equivalent yield.

EXAMPLE 2

This process is carried out in the same equipment used for Example 1, and the procedure is the same.

	Quantity	
Initial charge in reservoir, o-dichlorobenzene	55 lbs.	
m-Tolylene diamine in feed	16%	
Rate of addition of m-tolylene diamine	4.7 lbs./hr.	

	Temperature of m-tolylene diamine feed	110°C.	
	Rate of addition of phosgene	16 lbs./hr.	
	Rate of recycle feed through pump	8 gals./min.	
	Velocity in reaction zone, linear	3 ft./sec.	
5	Excess phosgene employed (above theory)	110%	5
	Temperature in reaction zone	165°C.	
	Temperature in reservoir kettle	165°C.	
	Pressure on reservoir kettle	Atmospheric	
	Pressure in recycle line	8 p.s.i. gauge	
10	Time of run	4 hours	10
	Yield of 2,4-tolylene diisocyanate	86.5%	

This example illustrates the use of increased concentration of m-tolylene diamine in o-dichlorobenzene and increased phosgene feed.

EXAMPLE 3

In this example the equipment and pro-

cedure of Example 1 are used. The temperature of reaction is lower and the rates of feed of m-tolylene diamine solution in o-dichlorobenzene and the phosgene feed are slower.

					<i>Quantity</i>	
20	Initial charge in reservoir, o-dichlorobenzene	55 lbs.	20
	m-Tolylene diamine in feed	8%	
	Rate of addition of m-tolylene diamine	2.85 lbs./hr.	
	Temperature of m-tolylene diamine feed	110°C.	
	Rate of addition of phosgene	9.5 lbs./hr.	
25	Rate of recycle feed through pump	8 gals./min.	52
	Velocity in reaction zone, linear	3 ft./sec.	
	Excess of phosgene employed (above theory)	106%	
	Temperature in reaction zone	140°C.	
	Temperature in reservoir	140°C.	
30	Pressure on reservoir kettle	Atmospheric	30
	Pressure in recycle line	8 p.s.i. g.	
	Time of run	4 hours	
	Yield of 2,4-tolylene diisocyanate	92%	

35 When the same process is run with a reaction zone temperature of 110°C. and a reservoir temperature of 110°C., a yield of 90.5% is obtained.

Where benzidine is substituted in the above process in place of the m-tolylene diamine, using a 12% solution in ortho-dichlorobenzene with a phosgene feed of 12 pounds per hour equivalent to an excess of 100% over theory, and the temperature in

both the reaction zone and the reservoir is maintained at 175°C. under a pressure in the reaction zone of 10 pounds per square inch, a high yield of 4,4'-diphenylene diisocyanate is obtained.

EXAMPLE 4.

Instead of the m-tolylene diamine of Example 3, methylene bis(4-phenylamine) is converted to the isocyanate under the following conditions:

					<i>Quantity</i>	
	Initial charge in reservoir, o-dichlorobenzene	55 lbs.	
	Concentration of amine in o-dichlorobenzene feed solution	12%	
	Rate of addition of the amine	3 lbs./hr.	
50	Temperature of amine feed solution	110°C.	50
	Rate of addition of phosgene	6 lbs./hr.	
	Excess of phosgene employed (over theory)	100%	
	Rate of recycle feed through pump	20 gals./min.	
	Velocity in reaction zone	7.5 ft./sec	
55	Excess of phosgene employed (over theory)	100%	55
	Temperature in reaction zone	175°C.	
	Temperature in reservoir	175°C.	
	Pressure in reaction zone	1 p.s.i. g.	
	Pressure in reservoir kettle	Atmospheric	
60	Time of run	5 hours	60
	Yield of methylene bis(4-phenyl isocyanate)	95%	

The throttle valve is not used in this run.

EXAMPLE 5

65 In this example, the apparatus employed

in the first four examples is modified by substituting a 4 inch diameter glass cylinder 4 feet long which serves as the reservoir in 85

place of the 10 gallon kettle. This reduces the total liquid holdup in the system to about 3 gallons. A tubular steel heat exchanger for heating is inserted in the reaction line between the amine feed inlet and the throttle valve. It has 5 square feet of heating surface. The linear pipe line distance from the amine feed line to the throttle valve is now about 6 feet. An inlet is placed in the recycle line ahead of the pump so additional solvent may be introduced.

This method of preparation differs from the previous examples in that an extra

quantity of o-dichlorobenzene is introduced into the recycled solution stream ahead of the recycle pump to decrease the concentration of the recycled 2,4-tolylene diisocyanate. The quantity introduced in this example is sufficient to reduce the diisocyanate concentration to 10% which is the equivalent to that obtained with an 8% m-tolylene diamine feed. The dilution permits the use of a 16% m-tolylene diamine feed without loss of yield due to formation of tars. The conditions are as follows:

15	Concentration of m-tolylene diamine in feed soln. ...	16%	15
	Rate of addition of diamine ...	3 lbs./hr.	
	Temperature of diamine feed solution ...	110°C.	
	Rate of addition of phosgene ...	10 lbs./hr.	
	Excess phosgene feed (over theory) ...	100%	
20	Rate of recycle feed through pump ...	8 gal./min.	20
	Rate of o-dichlorobenzene feed to recycle ...	22 lbs./hr.	
	Temperature in reaction zone ...	155°C.	
	Pressure in reaction zone ...	7 lbs./sq. in.	
	Pressure in reservoir ...	Atmospheric	
25	Time of run ...	3 hours	25
	Yield of 2,4-tolylene diisocyanate on diamine fed ...	93%	

EXAMPLE 6

The revised equipment of Example 5 is used with an additional change in the amine dispersing section. Instead of introducing the amine solution at a tee into a 1 inch pipe which gives a lineal velocity of 3 feet per second at a pump recycle of 8 gallons per minute, the amine solution is introduced

through a nozzle which is inserted at a 45° angle into a 3/8 inch inside diameter pipe through which the flow is at a lineal velocity of 20 feet per second at a pump recycle of 8 gallons per minute. This greatly increases the Reynolds number of the turbulent flow at this point.

The conditions of the run are as follows:

	Concentration of m-tolylene diamine in feed solution (o-dichlorobenzene) ...	16%	
	Rate of addition of diamine ...	3.3 lbs./hr.	
40	Temperature of diamine feed solution ...	110°C.	40
	Rate of addition of phosgene ...	10 lbs./hr.	
	Excess of phosgene feed over theory ...	85%	
	Rate of recycle feed through pump ...	8 gals./min.	
	Rate of o-dichlorobenzene feed to recycle ...	22 lbs./hr.	
45	Temperature in reaction zone ...	155°C.	45
	Pressure in reaction zone ...	7 lbs./sq. in.	
	Pressure in reservoir ...	Atmospheric	
	Time of run ...	3 hours	
	Yield of 2,4-tolylene diisocyanate ...	95%	

Using the same procedure as given in this example but with a pump that gave a recycle rate of 1 gallon per minute and a pressure in the reaction zone of 40 pounds per square inch with a temperature of 110° C., with no additional introduction of o-dichlorobenzene and using liquid phosgene, substantially the same yield of 2,4-tolylene diisocyanate was obtained.

EXAMPLE 7

The equipment of Example 6 and the same procedure is used except that no o-dichlorobenzene is fed into the recycle stream since the concentration of m-tolylene diamine in o-dichlorobenzene fed is only 8%. In this experiment a lower operating temperature is used.

60	Concentration of m-tolylene diamine in feed soln. ...	8%	95
	Rate of addition of diamine ...	3.3 lbs./hr.	
	Temperature of diamine feed solution ...	110°C.	
	Rate of phosgene feed ...	10.8 lbs./hr.	
65	Recycle rate ...	8 gals./min.	65

Temperature in reaction zone	90°C.
Pressure in reaction zone	6 lbs./sq. in
Time of run	3 hours
Yield of 2,4-tolylene diisocyanate	95.5%

5 As indicated in the above examples, it is usually desired to preheat the amine solution to assure complete solution of the amine before it is injected into the solvent solution of the phosgene. As also illustrated
10 in Example 6, the phosgene can be introduced in the liquid form as well as in the gaseous form since when viewed through a sight glass interposed in the line it appears to be completely soluble in the solvent
15 under the pressures used.

The advantage of the present process resides in the fact that much smaller equipment is required for any given rate of production, and, as illustrated in certain of the
20 examples, it is not necessary to use a large jacketed kettle where simple heat exchangers are employed. The process also has the advantage that the isocyanate is produced in a continuous manner and the time of
25 reaction of the amine with the phosgene in solution in the solvent requires only a fraction of a second.

What we claim is:—

1. In a process of manufacturing organic
30 isocyanates from organic amines and phosgene, the step which includes passing an inert solvent solution of an amine into an organic solvent solution of phosgene, at least 1.25 mols of phosgene being present
35 per equivalent $-NH_2$ group of the amine, the reaction being conducted under super-atmospheric pressure and under conditions of turbulent flow while maintaining the temperature above that at which the carbamyl
40 chloride of the particular amine employed is decomposed.

2. A process according to Claim 1 in which the temperature is maintained at from 90° to 180°C., and immediately flashing the
45 solution into a zone of lower pressure to liberate the hydrogen chloride and excess

phosgene from the solvent solution of the isocyanate that is formed.

3. A process according to Claim 1 or 2 after the formation of the isocyanate which includes a further step of recycling the solvent solution of the isocyanate with the continuous addition of phosgene and further
55 quantities of the inert solvent solution of the amine until the desired concentration of isocyanate in the solvent is obtained, and then continuously removing a portion of the isocyanate solvent solution from the system
60 while adding a sufficient amount of solvent to maintain a constant volume in the system.

A process according to any of Claims 1 to 3 in which 2,4-tolylene diisocyanate is
65 formed from m-tolylene diamine and phosgene, said tolylene diamine in an inert solvent solution being passed into the organic solvent solution of phosgene, the amount of phosgene employed being at least 25% in
70 excess of the stoichiometrical amount required for complete conversion of the diamine to the diisocyanate.

5. A process according to Claims 1 to 3 in which methylene bis(4-phenyl isocyanate) is
75 formed from methylene bis(4-phenylamine) and phosgene, said methylene bis(4-phenylamine) in an inert organic solvent solution being passed into the organic solvent solution of phosgene, the amount of
80 phosgene employed being at least 25% in excess of the stoichiometrical amount required for complete conversion of the diamine to the diisocyanate.

6. A process of manufacturing organic
85 isocyanates from organic amines and phosgene in accordance with Claim 1 substantially as set forth and described hereinbefore.

MARKS & CLERK.

763,535 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale.

